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## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Compositions comprising Biocidal Quaternary Ammonium Benzosulfimides

We, HOLLICHEM CORPORATION, a corporation organized and existing under the laws of the State of New Jersey, United States of America, of 840 Cooper Street, Camden, County of Camden, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to biocidally active compositions, and especially to such compositions which contain, as active ingredients, quaternary ammonium compounds.

It is well known that certain quaternary ammonium compounds are germicidal and fungicidal agents. Generally, however, these prior quaternaries are water-soluble and therefore utilizable only in disposable wash-waters and the like. Although certain quaternary ammonium benzosulfimides (quaternary ammonium saccharinates) were known to be water-insoluble they were hitherto considered useful only as impregnants for textile fabrics and similar solid materials.

We have now discovered that quaternary ammonium benzosulfimides and certain of their complexes can be effectively utilized as the biocidally active ingredient in compositions such as medicinal and cosmetic preparations, e.g. lotions, creams, sprays and dusting powders, where there is not necessarily a solid base material, and according to the invention we provide a biocidally active dispersible composition which comprises a carrier and a quaternary ammonium benzosulfimide or a halogen complex thereof homogeneously dis-

persed throughout the composition. It should be remarked that by the expression "dispersible composition" we mean not only liquids but also gels, granular powders and the like which are capable of flowing either immediately or upon being exposed to water or saliva, for instance as in the case of a lozenge.

The biocidally active compositions according to the invention have many applications. For example they may be used for cosmetic and medicinal purposes, as shaving creams and after-shave lotions, soothing, cleansing and cold creams, baby lotions, dust protectant and sun-tan creams, brilliantines and shampoos, face and talcum powders, deodorants, and eye and ear lotions. Furthermore, because of the sweetness of these compounds they are most appropriate for oral use since they obviate the necessity or minimize the difficulties of using additives to mask the disagreeable taste and irritating effects of the ordinary type of quaternary compounds. Thus they are suitable as toothpastes, toothpowders and mouthwashes.

The biocidal activity of the compositions of the invention also finds use in preventing biological degradation of petroleum, jet fuels, and lubricating oils, in which the compositions may be used as additives.

Apart from their biocidal properties the compositions of the invention also exhibit anti-static properties when used as a coating or incorporated into non-conductive substances. This makes them very useful for waxes and polishes for furniture, for example, and in the antistatic treatment of such materials as paper, furs and plastics. The various applications of the compositions according to the

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invention will be discussed in more detail below.

5 The quaternary ammonium benzosulfimides utilized herein may be prepared in known manner by reacting an aqueous solution of a selected quaternary ammonium halide with an aqueous solution of benzosulfimide or its sodium salt.

10 Illustrative of the quaternary ammonium benzosulfimides of the present invention are the alkyls such as cetyl trimethyl ammonium benzosulfimide and lauryl trimethyl ammonium benzosulfimide; the alkylaryls such as alkyl dimethyl benzyl ammonium benzo-  
15 sulfimide and lauryl dimethyl benzyl ammonium benzosulfimide; the N-alkyl-pyridiniums such as N-cetyl pyridinium benzosulfimide; the picoliniums such as myristyl gamma-picolinium; the groupings wherein the mole-  
20 cule contains an ester linkage, such as p-tertiary octylphenoxyethoxyethyl dimethyl benzyl ammonium benzosulfimide; groupings having oxygen in the form of amide or ester

linkages, such as N-(lauryl colamino formyl methyl)-pyridinium benzosulfimide and N-  
25 (myristyl colamino formyl methyl)-pyridinium benzosulfimide; those containing a sulfonamide group such as 2-phenyl-3-p-sulfamido-phenyl-5-undecyl-tetrazolium benzosulfimide and 4-sulfanilamido-benzyl tetradecyl dimethyl  
30 ammonium benzosulfimide; those containing a substituted aromatic nucleus such as lauryl-oxyphenyl trimethyl ammonium benzosulfimide, cetyl-amino-phenyl trimethyl ammonium benzosulfimide, and dodecyl-benzyl  
35 trimethyl ammonium benzosulfimide; the aliphatic and arylaliphatic isoquinoliniums such as lauryl isoquinolinium; the aliphatic and arylaliphatic morpholiniums such as N-dodecyl-N-methyl morpholinium benzosulf-  
40 imide; and the aliphatic and arylaliphatic imidazoliniums.

Illustrative of fluid or dispersible compositions according to the invention are the following Examples:

#### EXAMPLE 1

An antiseptic after-shave lotion:

Component	Parts by Wt.
ethyl alcohol	40.00
menthol	0.005
p-ethyl aminobenzoate	0.025
water	59.72
cetyl trimethyl ammonium benzosulfimide	0.25

50 The cetyl trimethyl ammonium benzosulfimide is mixed with the ethyl alcohol to form an alcoholic solution and this solution is then mixed with the menthol, p-ethyl amino-

benzoate and water; all the aforementioned intermixtures taking place at ambient temperature.

## EXAMPLE 2

An all-purpose soothing and biocidal cream:

Component	Parts by Wt.
stearic acid	15.0
beeswax (white)	2.0
lanolin (anhydrous)	1.0
mineral oil	23.0
G—1425 (polyoxyalkylene sorbitol-lanolin produced by Atlas Powder Co., Wilmington, Del.)	5.0
G—1441 (polyoxyalkylene sorbitol-lanolin produced by Atlas Powder Co., Wilmington, Del.)	1.0
Arlex (a non-crystallizing humectant solution containing 83% solids and consisting of sorbitol and related polyhydric materials, produced by Atlas Powder Co., Wilmington, Del.)	10.0
water	42.9
perfume	0.1
dodecyl benzyl trimethyl ammonium benzosulfimide	0.1

5 The stearic acid, beeswax, lanolin, mineral oil, G—1425 and G—1441 are mixed with the dodecyl benzyl trimethyl ammonium benzosulfimide and heated with constant agitation to 70° C. The Arlex and water are heated to 72° C, after being mixed together. The

second mixture is then added slowly and under continuous agitation to the first mixture while allowing the entire mixture to cool to ambient temperature. The perfume is added at 45° C. The mixture is then poured just before the setting point.

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## EXAMPLE 3

## A biocidally effective baby-lotion

Component	Parts by Wt.
stearic acid	4.0
lanolin (anhydrous)	2.0
sorbitan mono-oleate	0.5
polyoxyethylene mono-stearate	2.0
isopropyl palmitate	2.0
sorbitol syrup (70% by wt. sorbitol)	2.5
propylene glycol	2.5
water	84.4
perfume	0.1
alkyl dimethyl benzyl ammonium benzosulfimide	0.1

5 The first five components listed above comprise Mixture A. The next three components listed above comprise Mixture B. Mixture A is melted and the alkyl dimethyl benzyl ammonium benzosulfimide is added to the melt with constant agitation. The mixture is then heated to 90° C. Mixture B is heated

to 95° C and is then added to Mixture A with initial rapid stirring followed by slower stirring until the temperature drops to 55° C. The perfume is then added and the whole mixture is agitated slowly until it reaches ambient temperature.

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## EXAMPLE 4

A protective cream for use against dry dust and the like is prepared as follows:

Component	Parts by Wt.
stearic acid	15.0
Span 60 (Registered Trade Mark for sorbitan monostearate produced by Atlas Powder Co., Wilmington, Del.)	2.0
Tween 60 (Registered Trade Mark for polyoxyalkylene sorbitan monostearate produced by Atlas Powder Co., Wilmington, Del.)	1.5
zinc stearate	5.0
Arlex	5.0
methyl cellulose mucilage (4% in H <sub>2</sub> O—4000 cp.)	25.0
water	100.0
perfume	0.1
cetyl trimethyl ammonium benzosulfimide	1.0

5 All the fats including the zinc stearate are melted together and the cetyl trimethyl ammonium benzosulfimide is added to the melt which is then heated to 90° C. The Arlex is dissolved in the water and this aqueous solution is heated to 95° C. The aqueous solution is then added to the melt with rapid

agitation. After the temperature of the mixture has dropped to 55° C, the methylcellulose mucilage is worked in under moderate agitation. When the mixture has reached 40° C. the perfume is added. The product is then preferably packaged while still warm.

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## EXAMPLE 5

A biocidally effective brilliantine which is effective against dandruff is prepared as follows:

Component	Parts by Wt.
oleyl alcohol	18.0
ethyl alcohol	81.9
coloring (F.D.C. Yellow #3)	0.2
perfume	0.1
alkenyl dimethyl ethyl ammonium benzosulfimide	0.1

The alkenyl dimethyl ethyl ammonium benzosulfimide is mixed with the ethyl alcohol to form an alcoholic solution and this solution is intermixed with the other components at ambient temperature to form the finished product. 5

#### EXAMPLE 6

A biocidally active cleansing cream is prepared as follows:

Component	Parts by Wt.
paraffin wax	6.0
white beeswax	12.0
mineral oil	53.9
stearic acid	1.0
borax	1.0
water	25.5
perfume	0.5
lauryl isoquinolinium benzosulfimide	0.1

10 The paraffin wax, beeswax, mineral oil and stearic acid are mixed together and heated at 70° C until dissolved. The lauryl isoquinolinium benzosulfimide is added to the melt with rapid agitation. The borax is dissolved in the water and heated to 70° C and 15 is then added to the first mixture with constant agitation. The agitation is continued until the entire mixture reaches 45°—50° C at which point the perfume is added. As the mixture begins to thicken, it is poured into the molds or packages.

#### EXAMPLE 7

A biocidally active face powder is prepared as follows:

Component	Parts by Wt.
talc	49.9
rice starch	15.0
precipitated chalk	15.0
zinc oxide	15.0
zinc stearate	5.0
dodecyl benzyl trimethyl ammonium benzosulfimide	0.1

The above components are simply admixed at ambient temperature to form the granular composition.

## EXAMPLE 8

A biocidal cold cream is prepared as follows:

Component	Parts by Wt.
mineral oil	47.9
beeswax	6.0
spermaceti	6.0
cetyl alcohol	1.0
lanolin	1.0
water	38.0
perfume	0.1
alkyl dimethyl benzyl ammonium benzosulfimide	0.10

5 The mineral oil, beeswax, spermaceti, cetyl alcohol, and lanolin, together with the alkyl dimethyl benzyl ammonium benzosulfimide, are mixed together and heated to form a clear homogeneous liquid melt. After this mixture has cooled to 45°—50° C, this latter temperature is maintained while the water is added slowly and with continual stirring. The mixture is then cooled to 40° C with continuous stirring. At this time, the perfume is added and further cooling with continuous stirring is maintained down to 25°—30° C, at which time the product is ready for packaging. 10 15

## EXAMPLE 9

A very effective biocidal tooth powder is prepared in the following manner:

Component	Parts by Wt.
precipitated calcium carbonate	94.9
Powdered soap	5.0
cetyl trimethyl ammonium benzosulfimide	0.1

The above ingredients are admixed at ambient temperatures to form a granular composition ready for use.

## EXAMPLE 10

A biocidally active tooth paste is prepared as follows:

Component	Parts by Wt.
glycerin	23.0
gum tragacanth mucilage (5% in H <sub>2</sub> O)	14.0
precipitated chalk	49.9
bentonite	3.0
sodium lauryl sulfate	3.0
water	7.0
alkenyl dimethyl ethyl ammonium benzosulfimide	0.1

All of the above ingredients are thoroughly intermixed at ambient temperatures to form a homogeneous paste composition ready for use.

## EXAMPLE 11

A biocidally active foot cream is prepared as follows:

Component	Parts by Wt.
glyceryl monostearate (self-emulsifying)	15.0
lanolin	1.0
sorbitol syrup	2.5
glycerin	2.5
water	100.0
lauryl isoquinolinium benzosulfimide	0.25—0.50

- 5 The above components are thoroughly intermixed at ambient temperature whereby the quaternary compound is homogeneously dispersed through the cream which is formed.



## EXAMPLE 12

A biocidally effective foot powder is prepared in the following manner:

Component	Parts by Wt.
thymol	1.0
boric acid	10.0
zinc oxide	20.0
talc	68.9
dodecyl benzyl trimethyl ammonium benzosulfimide	0.1

These components are thoroughly inter- at ambient temperature to form the foot  
mixed and relatively dispersed with each other powder.

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## EXAMPLE 13

A sun-tan cream with biocidal properties is prepared as follows:

Component	Parts by Wt.
diethyleneglycol monostearate	2.0
stearic acid	1.5
cetyl alcohol	0.5
methyl anthranilate	5.0
triethanolamine	1.0
water	89.9
perfume	0.2
alkyl dimethyl benzyl ammonium benzosulfimide	0.1

The above components are intermixed at ambient temperature to form a homogenized cream.

## EXAMPLE 14

A biocidally active hair rinse is prepared in the following manner:

Component	Parts by Wt.
glyceryl monostearate	3.0
water	96.05
cetyl trimethyl ammonium benzosulfimide	0.95

The above components are thoroughly intermixed at ambient temperature to form the final product.

#### EXAMPLE 15

An antiseptic lozenge is prepared as follows:

Component	Parts by Wt.
sucrose	75.0
glucose solution in H <sub>2</sub> O (50% conc.)	24.0
glycerin	0.9
alkyl dimethyl benzyl ammonium benzosulfimide	0.1

5 The above ingredients are mixed and the stirring. It is then poured into molds and mixture is brought to the boil with constant allowed to harden.

#### EXAMPLE 16

A liquid shampoo with very satisfactory biocidal activity is prepared in the following manner:

Component	Parts by Wt.
coconut oil fatty acids	42.0
oleic acid	56.0
propylene glycol	55.0
triethanolamine	58.0
alkenyl dimethyl ethyl ammonium bensosulfimide	1.0

10 The fatty acids are intermixed. Then the amine is added and then the propylene glycol. The mixture is then stirred until a clear solution is obtained. Then the alkenyl dimethyl ethyl ammonium benzosulfimide is added. No heating is required and the mixing takes place at ambient temperature.

15 The mixture is then diluted with the water to any desired consistency. When the water

is initially added, the mixture assumes a petrolatum-like consistency but gradually changes to a clear, very slightly viscous solution of a pale amber color. If the solution becomes cloudy, more of the amine is stirred in, a little at a time, until the solution again becomes clear. Preferably a composition is obtained containing 3 parts by weight of water to 1 part by weight of the mixture listed above.

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## EXAMPLE 17

A biocidally active industrial cleaning composition is prepared as follows:

Components	Parts by Wt.
neutral toilet soap, preferably Na or K soaps of stearic, palmitic or oleic acids. ("neutral" meaning no excess alkali)	30.0
bentonite	30.0
sodium lauryl sulfate	10.0
lanolin	5.0
perfume	1.0
lauryl isoquinolinium benzo sulfimide	1.0

The bentonite and sodium lauryl sulfate are mixed together. The soap and lanolin are mixed with the lauryl isoquinolinium benzo-sulfimide and heated to about 70° C, after which they are mixed with the bentonite and sodium lauryl sulfate. The perfume is added as the mixture cools to ambient temperature. The product may then be pressed into cake form or 27 parts of corn meal may be mixed with 75 parts of the mixture to form a powdered soap.

## EXAMPLE 18

A biocidally active saponaceous mouthwash is prepared in the following manner:

Component	Parts by Wt.
neutral powdered soap of the same type as in Example 17	2.0
glycerin	15.0
alcohol	20.0
water	62.9
dodecyl benzyl trimethyl ammonium benzosulfimide	0.1

The above ingredients are intermixed at ambient temperature to form the completed mouthwash.

## EXAMPLE 19

A non-irritant shave cream is prepared as follows:

Component	Parts by Wt.
Coconut oil	10.0
castor oil	2.0
myristic acid	5.0
stearic acid	25.0
potassium hydroxide	9.5
borax	0.5
diglycol stearate	2.0
stearyl alcohol	1.0
liquid paraffin	1.5
sorbitol syrup	5.0
water	45.0
alkyldimethylbenzyl ammonium benzosulfimide	0.2

- 5 The myristic and stearic acids (without previous melting) are added to hot aqueous alkali (potassium hydroxide and borax solution at 80° C). After saponification, the remaining solid ingredients, including the alkyl dimethyl benzyl ammonium benzosulfimide, and the liquid paraffin are added and the mixture is stirred slowly. After the mixture is maintained at a temperature of about 80° C for an hour, the sorbitol syrup is added and the mixture is then allowed to cool to ambient temperature. 10

## EXAMPLE 20

A biocidally effective talcum powder is prepared in the following manner:

Component	Parts by Wt.
talc	69.9
magnesium stearate	5.0
starch	10.0
colloidal kaolin	15.0
cetyl trimethyl ammonium benzosulfimide	0.1

- 15 The above components are mixed dry at ambient temperature to form the finished product.

## EXAMPLE 21

A biocidally active antiperspirant and deodorant powder is prepared as follows:

Component	Parts by Wt.
talc	77.9
corn starch	10.0
sodium aluminum sulfate	2.0
salicylic acid	5.0
boric acid	5.0
alkenyl dimethyl ethyl ammonium benzosulfimide	0.1

The above ingredients are intermixed in the dry state at ambient temperature to form the final product.

## EXAMPLE 22

A biocidally effective eye lotion is prepared as follows:

Component	Parts by Wt.
boric acid	1.9
distilled water	98.0
cetyl trimethyl ammonium benzosulfimide	0.1

- 5 The above ingredients are intermixed at ambient temperature to form the final product.

## EXAMPLE 23

A biocidally active ear drop formulation is prepared as follows:

Component	Parts by Wt.
Maypon 4C (a protein condensation product with oleyl chloride: produced by Maywood Chemical Works)	1.0
water	98.9
alkyldimethyl benzyl ammonium benzosulfimide	0.1

The above ingredients are intermixed at ambient temperatures to form the finished product.

- 10 All of the above formulations are prepared at ambient pressures.

It is to be noted that the quaternary ammonium benzosulfimides disclosed and con-

templated herein can be utilized for both human and animal biocidal protection, the particular components and proportions being variable with the manner of use.

To illustrate the biocidal activity of the instant compounds at concentrations lower than 1%, a 0.75% by weight solution of lauryl

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isoquinolinium benzosulfimide in 90% isopropyl alcohol and a 0.75% by weight solution of alkyl dimethyl benzyl ammonium benzosulfimide in 90% isopropyl alcohol were prepared and used in separate bacteriostatic tests on separate batches of 1 inch cotton threads infected with *Salmonella typhosa*. At the same time, two separate batches of similarly infected 1 inch cotton threads were treated in separate tests with two separate controls consisting of pure 90% isopropyl alcohol.

The threads tested with the lauryl isoquinolinium benzosulfimide showed an inhibition zone of 7 mm., the threads treated with alkyl dimethyl benzyl ammonium benzosulfimide showed an inhibition zone of 4 mm., and the two isopropyl alcohol treated controls showed no inhibition whatsoever.

The advantage of the quaternary ammonium benzosulfimide-halogen complexes is that they have enhanced germicidal effects, but do not retain the undesirable properties of the halogens such as their relatively high toxicity and their tendency to irritate, stain and discolor both human skin and fabrics.

The quaternary ammonium benzosulfimide-halogen complexes are conveniently prepared by diluting the selected quaternary ammonium halide salt to 10% with deionized water. This 10% aqueous solution is heated to about 160° F. The selected halogen is then added slowly with rapid agitation. The halogen may also be added in the form of a complex, as for example in the case of iodine as a KI<sub>3</sub> complex. It may alternatively be added in the form of an alcohol solution or dissolved in some other suitable solvent. The aqueous solution of the quaternary ammonium-halogen complex is allowed to cool to 75° F at which temperature a stoichiometric amount of sodium benzosulfimide in a 10% aqueous solution is added.

In some instances the quaternary ammonium benzosulfimide-halogen complex separates as a solid and in others as a liquid. The isolation of the solid type of complexes is obviously quite simple. However, where the complexes are soluble in water or are themselves in liquid form, the isolation is more difficult. In the case of liquids, partially soluble in water, the organic material is salted out, the salt water-organic layers are separated and the liquid-organic layer is dried under reduced pressure in a forced draft oven.

Where the complex is completely water-soluble, the water must be removed by evaporation under reduced pressure or in a forced draft oven. The residue is taken up using a solvent such as isopropyl alcohol. The salt formed in the reaction is removed by filtration and the alcoholic solution of the complex recovered by evaporation.

The following Examples illustrate the preparation of the complexes contemplated by the present invention:

#### EXAMPLE 24.

380 grams of 50% aqueous solution of alkyl dimethyl benzyl ammonium chloride ( $\frac{1}{2}$  mol) were diluted to 10% solids with deionized water. The 10% aqueous solution was heated to 160° F and 28.5 grams of iodine crystals were added with agitation until the iodine was completely dissolved. The 10% quaternary ammonium iodine complex was allowed to cool to 75° F. 120 grams of sodium benzosulfimide ( $\frac{1}{2}$  mol) was dissolved in water to make a 10% aqueous solution and this latter solution was then added to the quaternary solution with rapid and vigorous agitation.

The quaternary benzosulfimide-iodine complex separated as a heavy reddish-brown crystalline mass. The supernatant water solution was decanted and the precipitate further washed with deionized water. The alkyl dimethyl benzyl ammonium benzosulfimide-iodine complex was then filtered and dried under reduced pressure. The theoretical content of the complex was 10% by weight iodine. By titration of sodium thiosulfate, the iodine content attained by the above process was 9.5% by weight.

#### EXAMPLE 25.

360 grams of a 50% aqueous solution of dodecyl benzyl trimethyl ammonium chloride ( $\frac{1}{2}$  mol) were diluted to 10% with deionized water. The 10% solution was then heated to 150–160° F. at which point 27 grams of bromine was added with vigorous agitation. The aqueous quaternary halide was then cooled to room temperature. 120 grams of sodium benzosulfimide ( $\frac{1}{2}$  mol) was dissolved in water to make a 10% solution. This latter aqueous solution was added to the aqueous quaternary-halogen complex solution with vigorous agitation. The mixture then separated into two layers. The quaternary-halogen complex was further separated by adding an excess amount of sodium chloride. The water layer was separated from the quaternary-halogen complex layer in a separatory funnel and the quaternary-halogen complex was then dried in a forced draft oven. The end product dodecyl benzyl trimethyl ammonium benzosulfimide bromine complex was a light yellow waxy material containing 10% by weight bromine.

#### EXAMPLE 26.

265 grams of a 50% aqueous solution of dodecyl trimethyl ammonium chloride ( $\frac{1}{2}$  mol) were diluted to 10% strength with deionized water. The solution was then heated to 150–160° F and 22 grams of bromine was added. The mixture was then cooled to room temperature. 120 grams of sodium benzosulfimide ( $\frac{1}{2}$  mol) was dissolved in water to make a 10% solution and this solution was added to the aqueous quaternary-halide complex solution with rapid agitation. The reaction mixture

remained clear and in a single phase. The total solution was then evaporated under reduced pressure. The residue was extracted with isopropyl alcohol, the salt filtered off and the alcoholic filtrate evaporated under reduced pressure. The end product was dodecyl trimethyl ammonium benzosulfimide-bromine complex.

#### EXAMPLE 27.

52 grams (0.1 mol) of stearyl trimethyl ammonium benzosulfimide were dissolved in 57 grams of 99% isopropanol. 5 grams of bromine were added with rapid agitation to form a 50% solution of stearyl trimethyl ammonium benzosulfimide-bromine complex containing a theoretical amount of 10% by weight bromine. The product was isolated by evaporating the alcohol under reduced pressure at 120° F.

#### EXAMPLE 28.

The same components and procedure was followed as in Example 27 except that the

product was isolated by diluting the alcoholic mixture with water up to approximately 1000 grams total, at which time the stearyl trimethyl ammonium benzosulfimide-bromine complex precipitated out as a light yellow crystalline material.

As an illustration of the biocidal properties of the compounds of the present invention, an aqueous wash solution having a concentration of 0.5 ppm alkyl dimethyl benzyl ammonium benzosulfimide-bromine complex containing 10% by weight bromine was found to be bacteriostatic against *Staphylococcus aureus*. The same type of wash solution, but with a concentration of 10 ppm of the quaternary, was found to be bacteriostatic against *E. coli* and *E. typhosi*.

As further illustrative not only of the biocidal properties but also of the compatibility with organic anionic detergents of the instant type of quaternary ammonium benzosulfimide-halogen complexes, the following liquid wash solution was prepared:

Component	% by Wt.
potassium tripolyphosphate	19.5
sodium tripolyphosphate	5.0
"Ultrawet 60L" (alkyl aryl sulfonate anionic detergent produced by Atlantic Refining Co., Phila., Pa.)	33.0
"Onyxol 336" (Lauric acid alkanolamine condensate; a liquid detergent produced by Onyx Oil & Chemical Co., Jersey City, N.J.)	5.0
carboxyl methyl cellulose	0.5
alkyl dimethyl benzyl ammonium benzosulfimide-bromide complex containing 10% by weight bromine	1.0

The above components were admixed with constant agitation and at ambient temperature and pressure. The resultant composition was then used on textiles in a conventional household clothes-washing machine. In bacteriostatic tests, a halo of 2 mm. against *E. coli* and 4 mm. against *Salmonella typhosa* were obtained. A halo of 6 mm. was obtained against *Staphylococcus aureus*.

In addition to the aforementioned biocidal activity, this composition also exhibited very satisfactory detergent activity, thereby illustrating the complete compatibility between the anionic surface-active agents and the quaternary-halogen complex.

In general, the quaternary ammonium benzosulfimide-halogen complexes are biocidally effective at concentrations of the halo-

gen ranging from less than 0.1% to about 20% by weight of the complex.

As mentioned above, the quaternary ammonium benzosulfimides of the present invention are also highly effective antistatic agents when used as a coating or incorporated into non-conductive substances. They are non-corrosive, not readily leached out by water and are not disagreeable to the senses such as taste, smell, etc.

The antistatic properties of the aforementioned quaternary ammonium benzosulfimides make them highly desirable in waxes and polishes for furniture, automobiles, floors, walls and the like. These waxes and polishes, when applied to the surfaces to be treated, not only provide an attractive and protective finish but also prevent the accumulation of dust, dirt,

grime and the like which would otherwise occur as the result of static electricity on these surfaces. Furthermore, there is no corrosive effect on the surfaces such as would be occasioned by the use of ordinary quaternary ammonium salts. In addition, the antistatic properties provided by many of these compounds, especially those which are water-insoluble, are relatively permanent even when the surfaces, such as automobile bodies, are exposed to heavy rains or washings.

The quaternary compounds utilized in the present invention are also valuable in the antistatic treatment of paper, textiles, skins, leathers, furs, plastics and other such electrically non-conductive materials. They are compatible with all these various materials and their compatibility with polymeric materials such as epoxy resins, phenolics, acrylates, cellulose esters, polyolefins, polyurethanes, polyvinyls and nylon makes them ideal for blending, impregnating or coating such materials. The blending, particularly, lends itself to a single-process manufacture since the quaternary can be intermixed with the polymeric materials and extruded, molded or cast together therewith into the final product.

The compositions of this invention find especial utility in the manufacture of products which are subject to oral use such as drinking cups, toothbrush handles and bristles, children's plastic toys and the like. The non-corrosive nature and agreeable taste of the quaternary ammonium benzosulfimides permit them to be readily used in such products for preventing the accumulation of dust, dirt, grease and grime. Furthermore, since these quaternaries are themselves highly active germicidal and fungicidal substances, even at very low concentrations, they serve the highly important dual functions of biocidal and dirt-preventative agent.

The quaternary ammonium benzosulfimides have active antistatic capabilities at relatively low concentrations down to about 1% by weight. Of course, the higher the concentration, the greater the antistatic properties.

The following Examples are illustrative of this aspect of the present invention:

#### EXAMPLE 29.

A 2% by weight solution of each of the following quaternary ammonium benzosulfimides in Epolene E (Registered Trade Mark for a pelletized, emulsifiable, relatively low molecular weight polyethylene wax produced by Eastman Chemical Products, Inc., Kingsport, Tenn.) were made:

- (1) alkyl dimethyl benzyl ammonium benzosulfimide
- (2) cetyl trimethyl ammonium benzosulfimide
- (3) dodecyl benzyl trimethyl ammonium benzosulfimide
- (4) alkenyl dimethyl ethyl ammonium benzosulfimide

#### (5) lauryl isoquinolinium benzosulfimide

Each of the aforementioned 2% solutions were made by melting together 5 gm. Epolene E and 100 mg. of the selected quaternary. In each case, when the entire mixture was molten, the ingredients thereof were intimately mixed and spread out in a layer or sheet. When cool, each sheet was utilized as a separate sample. A blank was also prepared in the same manner as the other samples except that the blank consisted only of 5 gm. Epolene E and had no quaternary component.

Each of the samples, including both the samples containing the quaternaries and the blank, were then treated by being rubbed briskly against a piece of cotton fabric and then being held about 4 mm. above a pile of cigar ashes. None of the five samples containing the quaternaries showed any evidence of static electricity since there was no adherence of the ashes. The blank, however, showed considerable static electricity since there was a large accumulation of adhered ashes thereon.

#### EXAMPLE 30.

Six sheets or samples of pure Epolene E were prepared, each sample weighing between 2 and 3 gm. each. Five of these samples were each surface coated with a different quaternary ammonium benzosulfimide selected from the following:

- (1) dodecyl benzyl trimethyl ammonium benzosulfimide
- (2) cetyl trimethyl ammonium benzosulfimide
- (3) alkyl dimethyl benzyl ammonium benzosulfimide
- (4) lauryl isoquinolinium benzosulfimide
- (5) alkenyl dimethyl ethyl benzosulfimide

After being surface-coated, each of the above five samples was washed rapidly with methanol to remove any excess quaternary. The surface coating on each sample weighed between 2 and 4 mg.

The five coated samples plus the sixth uncoated sample or blank were then each rubbed briskly against a piece of cotton fabric and held about 4 mm. above a pile of cigar ashes. There was no adhesion of ashes to any of the five coated samples. However, the uncoated blank had a large amount of ashes adhered thereto.

In addition to their antistatic properties, various of the quaternaries utilized in these Examples, such as the dodecyl benzyl trimethyl ammonium benzosulfimide, the alkyl dimethyl benzyl ammonium benzosulfimide and the lauryl isoquinolinium benzosulfimide, are completely water-insoluble, while the others are generally less water-soluble than the ordinary quaternary ammonium salts. These compounds are, therefore, either not at all or much less subject to leaching out when exposed to water than are the ordinary quaternary ammonium salts.



The compositions of the invention are also very advantageously used as additives in petroleum products where they function as biocidal agents to prevent biological degradation of the petroleum. For example, in jet fuels and the like, there is a danger of clogging during use because of the accumulation of fungi, bacteria and other such biological growth. In lubricating oils and the like, there are often present various additives such as soaps and detergents. These additives are often subject to breakdown because of the biological action of micro-organisms. The accumulation of the micro-organisms and their degradative action on soaps and other additives is substantially eliminated by adding small quantities of the present compounds, down to about 1% by weight, to the petroleum products.

Another important property of certain of the present compounds is their thixotropic quality. Only certain of the compounds, however, have this quality, these particular compounds being those wherein the quaternary radical has four alkyl groups attached to the nitrogen atom, one of these groups being a long-chain group having at least 14 carbon atoms in the chain and the other three groups being lower alkyls having no more than 5 carbon atoms in the chain. These thixotropic type quaternary ammonium benzosulfimides not only act as active biocidal agents but also have very effective thickening action whereby they increase the viscosity of any water-based composition and prevent settling or precipitating out of both themselves and other ingredients such as pigments, fillers and the like. In fact, the greater the dilution of the composition with water, the greater the viscosity becomes when these particular type compounds are present.

#### WHAT WE CLAIM IS:—

1. A biocidally-active dispersible composition comprising a carrier and a quaternary ammonium benzosulfimide or a halogen complex thereof homogeneously dispersed throughout the composition.
2. A composition according to claim 1 wherein the quaternary ammonium benzosulfimide or halogen complex thereof is present in an amount of 0.5 to 10 ppm. of the carrier.
3. A composition according to claim 1 or 2 wherein the quaternary ammonium benzosulfimide or complex comprises less than 1% by weight of the composition.

4. A composition according to any of the preceding claims wherein the quaternary ammonium benzosulfimide or complex is water-soluble.

5. A composition according to any of claims 1 to 3 wherein the quaternary ammonium benzosulfimide or complex is water-insoluble.

6. A composition according to any of the preceding claims comprising also a cleansing agent.

7. A composition according to any of the preceding claims wherein the composition is a liquid composition.

8. A composition according to any of claims 1 to 6 wherein the composition is a granular composition.

9. A composition according to any of claims 1 to 8 wherein the halogen comprises between 0.1 and 20% by weight of the complex.

10. A composition according to claim 9 wherein the halogen comprises substantially 10% by weight of the complex.

11. A composition according to claim 6 wherein the cleansing agent is admixed with an anionic detergent.

12. An electrically non-conductive substrate, having a coating of a composition as claimed in claim 1.

13. An article made from an organic polymer, having coated thereon or blended therewith a composition as claimed in claim 1.

14. A polishing wax comprising a composition according to claim 1.

15. A petroleum product comprising a composition according to claim 1.

16. A composition according to any of claims 1 to 11 wherein the quaternary ammonium benzosulfimide has four alkyl groups attached to the nitrogen atom of the quaternary ammonium radical, one of the groups being a long chain alkyl group having at least 14 carbon atoms in the chain and the other three groups being alkyl groups having from 1 to 5 carbon atoms in the chain.

17. A biocidally-active dispersible composition as claimed in claim 1 substantially as described in any one of Examples 1 to 23, 29 and 30.

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